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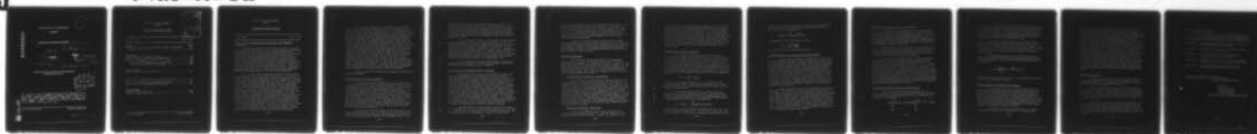
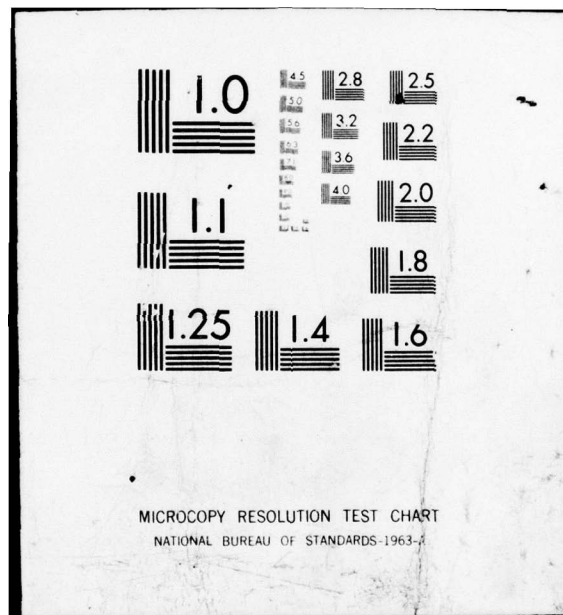UNCLASSIFIED   ESN-8-13   NL

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EUROPEAN SCIENTIFIC NOTES

1 July 1954   No. 8 - 13

AMERICAN EMBASSY   LONDON, ENGLAND

THE ELECTRICAL PROPERTIES AND STRUCTURE OF HEXAGONAL SELENIUM

Extensive investigations have been carried out on the electrical properties of pure, polycrystalline hexagonal selenium by L. M. Nijland in the Philips Laboratories (Eindhoven) and the results have recently been submitted for a doctorate in physical chemistry at the University of Amsterdam under the sponsorship of Prof. J.A.A. Ketelaar. The results obtained lead to a model of polycrystalline selenium consisting of well conducting crystals embedded in poorly conducting layers of amorphous selenium. While the structure of these layers cannot be elucidated in detail they probably consist of loose selenium chains. This model resembles the structures of several oxidic semiconductors previously investigated in the Philips Laboratories.

As is well known, various impurities can be added to selenium to change its conductivity and the mobility of holes therein. The conductivity increases upon addition of bromine and decreases enormously in the presence of thallium as impurity. Using radioactive thallium Tl^{204} the mobility of thallium in selenium was determined and, in agreement with previous investigators, was found to be quite large. The rate of migration of thallium ions in selenium was observed to depend to a remarkable extent on the density of the selenium samples; the electro-diffusion, i.e., the diffusion under the influence of an applied field of some hundreds v/cm, increases tenfold upon going from selenium of density 4.80 to selenium of density 4.78. Various observations on the electrical properties can be adequately explained by assuming that thallium diffuses along the grain boundaries of polycrystalline selenium and builds up insulating layers between them. Thus the dc resistivity of such materials is very high and is localized in these layers; these will be shortcircuited by high frequencies at which accordingly a very much lower resistance is observed.

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The density of the charge carriers was studied by measurements of the Hall effect; the Hall coefficient was always positive showing that the current is primarily carried by holes. Both pure and bromine-containing samples of high density polycrystalline hexagonal selenium were investigated and the calculated density of holes was found to be only slightly dependent on the temperature and on the bromine content. The results indicate that there is about one hole in the sample for every 2×10^6 selenium atoms and their mobility varied between 0.06 and 2.2 cm^2/v sec, under the different bromine concentrations studied. It was shown that the theory which was used to interpret measurements of carrier mobility in germanium and in silicon leads to anomalous results in this case: calculating the mean free path of the carriers a distance of about 0.6A is obtained for room temperature, which is, of course, very much shorter than the spacing of the selenium atoms, 2.36A. The layer model mentioned above is capable of interpreting the results and leads to calculated mobilities in good agreement with experiment. The electrical behavior of selenium-tellurium alloys further confirms this model. The whole range of compositions was investigated and up to about 15 per cent tellurium the alloys behaved in a manner similar to pure selenium.

Full details of this work will appear in the Philips Research Reports.

ISOTOPE EFFECT IN BINARY MIXTURES

A relatively simple approach to the isotope effect in binary mixtures is being investigated in detail by Prof. I. Prigogine and his collaborators (Brussels). It is essentially based on their recent work on the cell model of liquids and solutions. Binary mixtures of the various isotopes of hydrogen and mixtures of He^3 with He^4 represent interesting systems in which quantum effects are of dominating importance. This is primarily due to the fact that the wave character of these molecules plays a significant role, even on a macroscopic scale. In the case of isotopic mixtures of the heavier elements, the Brussels group finds that the difference in zero point energy is the main source of deviation from ideality, and can lead to small effects, of the order of 0.1 cal/mole.

In the case of the mixtures of the very light isotopes mentioned above; perhaps the simplest phenomenological description of the approach used by Prigogine is to consider that the mixing process involves the components under such

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pressures that there is no volume change on mixing. It is assumed that the zero point energies depend only on the effective volume per particle and on the mass of the particle in the cell. The treatment developed yields the excess thermodynamic properties as a function of the compressibilities and of the volumes of the pure components and the calculated results are in good agreement with available experimental data.

It is interesting that the calculated volume change on mixing changes signs at a certain reduced mass of the system; thus the calculated volume change is positive for T_2 + D_2 and for HD + H_2, in agreement with experiment and a positive volume effect is predicted for H_2 + D_2. Approximately 1 per cent contraction is, however, predicted for the equimolar mixing of He^3 + He^4. In view of the fact that there are no particular experimental difficulties in the way of such measurements, it is to be hoped that these predictions will soon be subjected to experimental test.

It is planned to publish full details of these investigations in Physica in the not too distant future (cf. also Advances in Physics, 3, 131 (1954)).

A NEW TYPE OF INFRARED ABSORPTION PROCESS

An interesting new type of absorption process was recently observed in the laboratories of Prof. J.A.A. Ketelaar (Amsterdam) in the course of their continuing investigations on the infrared absorption spectra of gases at high pressures. In observing the infrared absorption in equimolar mixtures of carbon dioxide plus nitrogen, carbon dioxide plus oxygen, and oxygen plus nitrogen, at pressures of the order of 150 atmospheres, bands are observed which appear to correspond to the simultaneous absorption of one quantum by each of the two species present. Such a "mixed" combination band is somewhat surprising, since consideration of the intermolecular forces does not suggest the presence of a minimum in the potential energy diagram. It is hoped that study of the intensities of these bands, which occur in the region of 1.2 - 1.4 μ, may give some information regarding the structure of the "complex" involved and the distances of approach of the participating species.

The experimental arrangement is relatively simple. A 1 m steel tube is used as the pressure vessel and the rocksalt windows, of 15 mm thickness, are fitted loosely in such a manner that it is the pressure inside the tube which

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presses them tightly against the supporting steel frame. The optical arrangement is such that by means of one plane and one focusing mirror the image of the exit window is focused into the precise location of the infrared source of a conventional Perkin-Elmer instrument. Thus no changes are necessary in the infrared spectrograph itself and it can be readily adapted from these measurements to conventional liquid or gas spectroscopy.

In view of the well known solvent power of high pressure gases, particular attention was paid to the presence and possible effect of impurities. Perhaps the most convincing argument in favor of the above interpretation of the newly observed bands is the dependence of their intensities on the square of the pressure.

OXIDATION PROCESSES

Two Dutch and two British Chemical Engineering Societies held a joint Conference on Oxidation Processes recently in Amsterdam. An interesting general feature of the contributions, which were largely of a review nature, was the fact that a large proportion of the oxidation processes discussed involved the use of metal or metal oxide catalysts. The oxidizing agent was either pure oxygen or air in all but one of the processes discussed.

Vanadium Oxide Catalysts in Oxidations

The structure of crystalline vanadium pentoxide led P. Mars and D. W. van Krevelen (Geleen) to attribute its catalytic action to certain oxygen ions; in this lattice two kinds of oxygen ions can be distinguished. The rate of oxidation of aromatic hydrocarbons with this catalyst depends on the concentration of those oxygen ions which lie in planes parallel to those defined by the vanadium ions, and on the amount of aromatic material adsorbed on the surface. At high partial pressure of oxygen and/or low partial pressure of the aromatic, the color of the catalyst will be yellowish brown; at low partial oxygen pressure and/or high partial pressure of the aromatic the color of the catalyst changes to greenish blue and analysis shows the presence of high concentrations of tetravalent vanadium.

Oxidation of Olefins to Epoxides

G. H. Twigg (Epsom) gave a detailed account of liquid phase oxidation in terms of the free radical chain mechanism proposed by Bolland. A point of interest which

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emerged from his considerations regarding the oxidation of paraffins is that in general this will not lead to any one major product unless the structure of the molecule induces preferential attack at one position. Dr. Twigg reported work on the oxidation of a number of olefins yielding the olefin epoxide as the major product. It was found that the addition of suitable catalysts to the oxidation of olefins increases both the rate of oxidation and the rate of production of epoxide. This suggests that the epoxide is not formed by the interaction of a hydroperoxide molecule with the olefin but rather through attack of radicals on the double bond.

SECOND COEFFICIENT OF VISCOSITY

At a recent discussion-meeting of the Royal Society on the first and second coefficients of viscosity of fluids, Sir Geoffrey Taylor of Cambridge University presented the results of a simplified theory for an incompressible fluid containing gas bubbles. In such a fluid the compressibility comes only from the compressibility of the gas bubbles. With the simplifying assumptions that the gas has zero viscosity and that the proportion v of the total volume which is occupied by the bubbles is small, the result for the macroscopic second coefficient of viscosity is

$$\mu' = \lambda + \frac{2}{3}\mu = \frac{4}{3}\frac{\mu}{v}$$

where μ is the shear coefficient of viscosity for the incompressible fluid. The singular behavior of this expression comes from the assumption that the basic fluid is itself incompressible.

At the same meeting Prof. J. Meixner of the Technical Institute of Aachen discussed the relationship between an after-effect theory and a thermodynamic theory having a second viscosity. The after-effect theory which he considers has as its basis the equation

$$\sigma_i = C_{ik}\epsilon_k - \int_0^\infty C_{ik}(u)\,\epsilon_k(t-u)\,du$$

where the σ_i are the stress components and the ϵ_k the velocity gradient components, and C_{ik} and $C_{ik}(u)$ are viscosity tensors. The relation between this approach and the

thermodynamic theory appears in the form the after-effect theory must take in order for the two to be identical. With the Laplace transformation

$$\Gamma_{ik}(p) = \int_o^\infty C_{ik}(u)\, e^{-pu}\, du$$

the quantities Γ_{ik} must have the form

$$\Gamma_{ik} = \sum_\gamma \frac{R_{ik\gamma}}{1 + \tau_\gamma p}$$

where the τ_γ are the relaxation times.

URINARY EXCRETION OF ENZYMES IN CANCER PATIENTS

In Prof. Eric Boyland's laboratory at the Chester Beatty Research Institute, London, studies are being made on the urinary excretion of enzymes which split detoxified o-aminophenols. These phenols are ordinarily excreted as the sulfates or glucuronides. These are non-carcinogenic while the free o-amino phenols are carcinogenic. Using 24 hour urine samples it has been found that humans with multiple tumors of the bladder have a many-fold increased excretion of both a sulfatase and a glucuronidase capable of splitting the corresponding detoxified phenols. Individuals who have had bladder tumors removed (and are tumor free) show a decreased excretion of these enzymes but do not return to normal. Persons suffering from other forms of neoplasm show no significant elevation of the urinary level of these enzymes.

There is doubt as to the cause-effect relationship involved. The absence of high enzyme excretion in any of the normal series and the persistence of elevated excretion in persons from whom tumors of the bladder have been removed might seem to argue for the elevated excretion being an effect of the tumor growth. However, the series of normal individuals is too small to exclude the possibility that a small fraction of the population has a high level of excretion of these enzymes before any tumors of the bladder appear. One possible hypothesis is that such individuals exist and by liberating free o-amino phenols in the bladder are predisposed to tumor development.
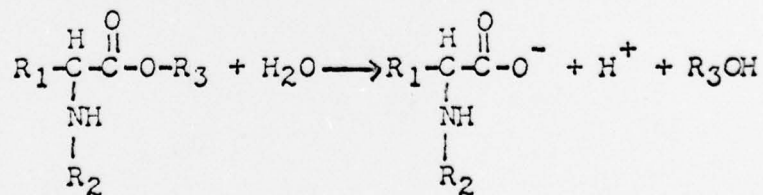
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CYTOLOGICAL EFFECTS OF RADIOMIMETIC DRUGS

Prof. Peo Kollar of the Chester Beatty Research Institute continues to be interested in the effects of radiomimetic drugs on the karyokinetic process. A variety of agents including the nitrogen mustards /̲ bis- (β-chloroethyl) amines/ and diepoxides produce "stickiness" or non-disjunction of chromosomes leading to abnormal anaphase figures. Lagging chromosome pairs may be isolated at telophase to form micronuclei.

Because of the effectiveness of the epoxides and certain aromatic nitrogen mustards which do not cyclize to ethylene immonium cations, there seems doubt that the alkylation hypothesis regarding nitrogen mustard action can be regarded as universally applicable.

It has also been demonstrated in Prof. Kollar's laboratory that root tip cells of Vicia faba are most sensitive to the cell division blocking action of the nitrogen mustards shortly after a mitosis. This is to be contrasted with the action of x rays which are most effective when used late in the intermitotic interval. The early sensitivity and late resistance to division block by the nitrogen mustards can be used to account for the delay in division block commonly noted when populations of cells are exposed to nitrogen mustards. Presumably those cells in the population which divided some time ago are the ones which proceed to division. This has previously been postulated but the findings noted above provide direct experimental evidence bearing on the point.

KINETICS OF HYDROLYSIS OF AMINO ACID ESTERS

Dr. Herbert Gutfreund of the Department of Colloid Science, Cambridge, is investigating the kinetics of hydrolysis of esters of amino acids as catalyzed by trypsin. The reaction is

$$R_1-\underset{\underset{R_2}{\overset{|}{NH}}}{\overset{H}{\underset{|}{C}}}-\overset{O}{\overset{||}{C}}-O-R_3 + H_2O \longrightarrow R_1-\underset{\underset{R_2}{\overset{|}{NH}}}{\overset{H}{\underset{|}{C}}}-\overset{O}{\overset{||}{C}}-O^- + H^+ + R_3OH$$

R_1 is the residue of lysine or arginine, R_2 ethyl or methyl to satisfy the specificity requirement of trypsin that the amino group be substituted, and R_3 has thus far been methyl or ethyl. The generation by a hydrion in the course of the reaction permits following the time course by pH change. Nitrophenols of appropriate pK' are used as calorimetric indicators at or near pH = pK'.

A solution of the ester and a solution of the enzyme are virtually instantaneously (ca 1 millisecond) injected into a reaction chamber with turbulent mixing. Light passing through the reaction mixture falls on a photomultiplier tube. The output of the photomultiplier tube is led to a cathode ray oscilloscope the beam of which is photographed.

The reaction requires about 20 milliseconds to achieve the steady state and Dr. Gutfreund hopes to be able to calculate all of the pertinent reaction constants for the reactions

$$E + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ES \xrightarrow{K_2} E + P$$
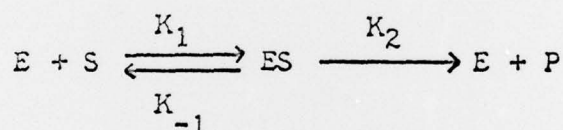
In particular he hopes to be able to calculate K_1 from the form of the acceleration curve.

HEALTH HAZARDS IN UNDERGROUND FACTORIES

At the Annual Meeting of the Ergonomics Society recently held at Leamington Spa, England, papers were presented on the physiological and psychological effects of work in high-temperature environments, health hazards of work in underground factories, attitudes of workers doing repetitive tasks, applications of psychology in small industry, and development of psychological methods for the study of problems in industry. The proceedings have been described in Technical Report ONRL-44-54; one of the contributions is summarized in the following.

S. Forssman, World Health Organization, Geneva, reported the results of a study made of the health of

workers in underground factories in Sweden. The study was
carried out by the Department of Occupational Health,
National Institute of Public Health; it was undertaken be-
cause of numerous complaints of illness made by workers in
underground factories. Questionnaires were sent to workers
in seven factories, three underground and four on the
surface. The factories were chosen so as to equate, as
nearly as possible, the surface and underground groups with
regard to such factors as age distribution, social back-
ground of workers, and nature of work. The results obtain-
ed by the questionnaires and follow-up studies showed that,
compared with workers in surface factories, workers in
underground factories tend to complain more often of ail-
ments such as fatigue, headache, sleepiness and eye strain.
Frequency of absences from work was found to be higher
among underground workers but the average number of days
lost due to sickness was higher for the surface workers.
No evidence was found to support the hypothesis that there
are special health hazards related to work in underground
factories. However, some workers do blame many of their
personal difficulties, problems, and minor ailments upon
assumed health hazards of the underground working environ-
ment.

PERSONAL NEWS ITEMS

The newly created Cripps Chair of Metallurgy at
Nottingham University is to be occupied, starting this
September, by Dr. J. W. Cuthbertson, assistant director of
research of the Tin Research Institute.

Prof. William Burns, Department of Physiology,
Charing Cross Hospital Medical School, London University,
will spend the summer doing research on the physiology of
hearing at the Central Institute for the Deaf in St. Louis,
Missouri. Prof. Burns' trip is sponsored by the Medical
Research Council of Great Britain and by the Central Insti-
tute for the Deaf.

Sir Frederic Bartlett, retired Professor of Psy-
chology, Cambridge University, and Prof. Roger Russell,
University College, London University, are attending the
International Congress of Psychology in Montreal, Canada,
7 - 12 June. Prof. Russell will remain in the United
States for several months to work on an American research
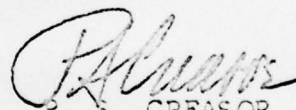project.

TECHNICAL REPORTS OF ONRL

The following reports have been forwarded to ONR, Washington. Copies may be obtained by addressing requests to the Commanding Officer, Office of Naval Research Branch Office, Navy No. 100, c/o Fleet Post Office, New York, N.Y.

ONRL-36-54   "Faraday Society Discussion on the Study of Fast Reactions" by G. J. Szasz

ONRL-37-54   "Psychological Research in Germany, France, and Belgium" by W. D. Neff

ONRL-38-54   "Belgian Research in Bacteriology and Parasitology" by T. K. Ruebush

ONRL-41-54   "Research in Tropical Medicine and Parasitology in The Netherlands" by T. K. Ruebush

ONRL-43-54   "The Annual Conference of the British Psychological Society" by W. D. Neff

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